UNCLASSIFIED

AD 419774

DEFENSE DOCUMENTATION CENTER

FOR

SCIENTIFIC AND TECHNICAL INFORMATION

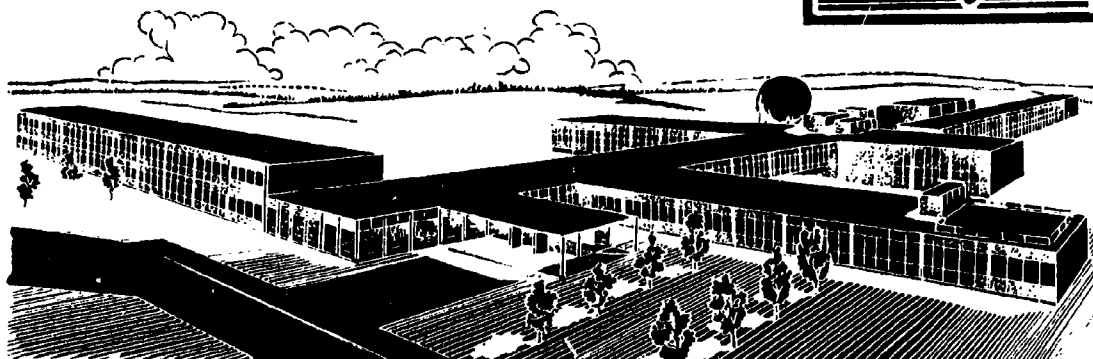CAMERON STATION, ALEXANDRIA, VIRGINIA

UNCLASSIFIED

ARL 63-160

PHYSICAL AND PREPARATIVE STUDIES OF TRANSITION METAL CHELATES

R. D. ARCHER

*UNIVERSITY OF CALIFORNIA
RIVERSIDE, CALIFORNIA*

SEPTEMBER 1963

NOTICES

When Government drawings, specifications, or other data are used for any purpose other than in connection with a definitely related Government procurement operation, the United States Government thereby incurs no responsibility nor any obligation whatsoever; and the fact that the Government may have formulated, furnished, or in any way supplied the said drawings, specifications, or other data, is not to be regarded by implication or otherwise as in any manner licensing the holder or any other person or corporation, or conveying any rights or permission to manufacture, use, or sell any patented invention that may in any way be related thereto.

- - - - - - - - -

Qualified requesters may obtain copies of this report from the Defense Documentation Center, (DDC), Cameron Station, Alexandria, Virginia.

- - - - - - - -

This report has been released to the Office of Technical Services, U.S. Department of Commerce, Washington 25, D.C. for sale to the general public.

- - - - - - - -

Copies of ARL Technical Documentary Reports should not be returned to Aerospace Research Laboratories unless return is required by security considerations, contractural obligations or notices on a specified document.
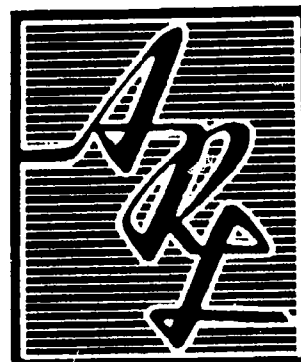
ARL 63-160

PHYSICAL AND PREPARATIVE STUDIES OF TRANSITION METAL CHELATES

R. D. ARCHER

UNIVERSITY OF CALIFORNIA
RIVERSIDE, CALIFORNIA

SEPTEMBER 1963

FOREWORD

This final report was prepared by the University of California, Riverside, California, on Contract AF 33(657)-9035 for the Aerospace Research Laboratories, Office of Aerospace Research, United States Air Force. The research reported herein was accomplished on Task 7023, "Chemical Research on Matter" of Project 7023-02, "Research in Analytical and Inorganic Chemistry" under the technical cognizance of Lt. B. W. Ponder of the Chemistry Research Laboratory of ARL.

The report includes exploratory research on some new molybdenum chelates (Part I), some α,β-unsaturated-β-ketoamine complexes (Part II), and some tungsten complexes (Part III). A published research paper, "The Preparation and Properties of Bis-(4-amino-3-pentene-2-ono)-nickel(II)" which appeared in the Inorganic Chemistry, 2, 292 (1963) is an addendum to the report.

The intermittent help of several undergraduates; namely, Miss Marilyn Bagwell, typist and laboratory helper; Mr. Warren C. Easley, laboratory helper; and Mssrs. Christopher Hills and Richard Lutz, undergraduate research students; is most gratefully acknowledged as is the support, both monetary and scientific, of the chemists of the Chemistry Research Laboratory, Aerospace Research Laboratories.

ii

ABSTRACT

The preparation of tris-(acetylacetonato)-molybdenum(III), dioxobis-(acetylacetonato)-molybdenum(VI) and the corresponding β-ketoamine complex, some eight-coordinate molybdenum complexes, trans-bis-(4-amino-3-pentene-2-ono)-nickel(II), and several tungsten complexes are described as are some of their properties. A novel preparation of tris-(acetylacetonato)-iron(III) is also indicated. Two new molybdenum complexes with the ethylenedinitrilotetraacetato ligand are noted but are incompletely characterized.

TABLE OF CONTENTS

ADDENDUM: "The Preparation and Properties of
Bis-(4-amino-3-pentene-2-ono)-nickel(II)," by
Ronald D. Archer, Inorganic Chemistry, 2, 292 (1963).

PART I. MOLYBDENUM CHELATES

INTRODUCTION

Completely chelated molybdenum is a rarity. Almost all of the large number of molybdenum chelates[1] are only partially chelated and may be catagorized as [Mo$_a$(monodentate)$_b$(chelate)$_c$]^d in which the monodentate group is oxo, chloro, carbonyl, nitrosyl, etc; the chelate is a polydentate ligand with oxygen, nitrogen, or sulfur donors; a, b, and c are integers; and d is the charge on the complex, normally negative or zero. Even preparation of molybdenum chelates in alcohol and ether yields oxo complexes.[1b]

Aminocarboxylic acids capable of sexadentate, octodentate, and decadentate coordination (ethylenedinitrilotetraacetic acid [H$_4$-edta], diethylenetrinitrilopentaacetic acid [H$_5$dtpa], and triethyl-enetetranitrilohexaacetic acid [H$_4$ttha], respectively) yield oxo complexes with two metal atoms per ligand, rather than forming 1:1 completely chelated compounds with molybdenum(V) and -(VI).[2] Polarographic evidence of a molybdenum edta complex in an oxidation state lower than five could not be obtained.[3] This probably means that no complexes with a metal to ligand ratio of 2:1 exist below an oxidation state of five. Therefore it seemed desirable to investigate the possibility of forming 1:1 molybdenum edta complexes by starting with low oxidation state complexes of molybdenum.

At the time this study was initiated, the only β-diketone complexes of molybdenum were partially chelated ones: namely, [MoO$_2$(acac)$_2$],[4] MoO(acac)·2.5H$_2$O,[5] MoO$_2$(acac),[5] and Mo(OH)$_3$(acac)$_2$-·3H$_2$O,[6] where acac indicates the anion of acetylacetone or 2,4-pen-tanedione. An early report of completely chelated [Mo(acac)$_2$][7] was later shown to be identical with [MoO$_2$(acac)$_2$].[5] In-as-much as most metals form completely chelated β-diketone complexes,[8] one of the objectives of this study has been the synthesis of a completely che-lated β-diketone complex of molybdenum. This objective has been realized as noted below.

RESULTS

Tris-(2,4-pentanediono)-molybdenum(III) has been prepared in aqueous solution under an inert atmosphere by two procedures.

(1) Oxygen free, aqueous solutions of K$_3$[MoCl$_6$] or (NH$_4$)$_2$-[Mo(H$_2$O)Cl$_5$], which had been prepared and isolated by electrolytic reduction of aqueous hydrochloric acid-molybdate(VI) solutions using standard procedures,[9] were mixed with ethanolic acetylacetone and benzene. The two phase system was vigorously stirred and heated under reflux conditions for two hours after which the benzene layer was concentrated, cooled, and petroleum ether added to precipitate the red chelate. However, oiling often occurred and attempts to chromatograph the product on alumina led to the isolation of Al-

$(acac)_3$ and a molybdenum oxide deposit on the column.

(2) Alternatively, an aqueous solution of $K_3[MoCl_6]$ was treated with acetylacetone and the chelate precipitated directly. This procedure involves heating the solution at 50-60° for two hours or letting the solution stand overnight at room temperature. Practically identical procedures have been published during the progress of this study.[10] (Preparation of the chelate from $Mo(CO)_6$ also has been reported recently.[10a, 11])

The air-sensitive, maroon complex has been found to be paramagnetic (3.9 Bohr magnetons) and to possess two ligand field absorption bands as expected for an octahedral d^3 complex with only slight trigonal distortion. The complex is susceptible to rapid air oxidation and requires careful handling in an inert atmosphere. Resolution of the complex into two optically active isomers should be possible, but has not yet been accomplished.

The brown oxidation product of $[Mo(acac)_3]$, which Larson and Moore[10a] have formulated as a more stable isomer of $[MoO_2acac_2]$, a well known yellow complex has also been prepared. However, the analyses obtained always are high in carbon and even higher in hydrogen, such that the emperical formula is approximately $MoO(OH)-(acac)_{2.2}$. The infrared spectra of the complexes have been compared by Larson and Moore,[10a] but magnetic and other spectral data seem desirable before a conclusion can be reached as to the nature of the oxidation product.

Dioxobis-(2,4-pentanediono)-molybdate(VI) was prepared by allowing MoO_3 to react with acetylacetone under reflux conditions for about 24 hours, and then adding petroleum ether to precipitate the complex, similar to the published procedure of Fernelius, Terada, and Bryant.[12] This complex decomposes slowly even at room temperature in the absence of excess acetylacetone which appears green and eventually blue. This decomposition has been followed using infrared spectroscopy which indicates no new complexes have been formed, but since the final product appears to be molybdenum blue some decomposition of the β-diketone must occur. Gas chromatographic analysis of the decomposition products is still in progress.

The corresponding unsaturated β-ketoamine complex of molybdenum-(VI) was prepared using a procedure similar to that noted above for the β-diketone complex with a reaction temperature of 150°. A cream colored precipitate was obtained by concentration of a petroleum ether solution of the crude product. One sample of the complex decomposed during vacuum filtration at room temperature and another decomposed under purified petroleum ether. However, the complex appeared stable in the presence of excess ligand. Because of its instability, the complex was not investigated further.

We have observed the formation of a green complex when Na_2H_2-edta and K_3MoCl_6 are allowed to react in air-free water. Interestingly enough, the complex is diamagnetic, suggesting that either

an oxidation-reduction reaction or a dimerization (similar to that in $K_3W_2Cl_9$) has occurred. The insoluble green product was found to be contaminated in the present method of preparation, but its insolubility and that of the contaminant have hindered purification. The complex is easily oxidized to a brown product still uncharacterized.

The use of dimethylsulfoxide (DMSO) as a solvent for preparing low valent complexes of molybdenum has given some interesting results. It has been found that potassium hexachloromolybdate(III) is soluble in dimethylsulfoxide; however, chelation reactions are complicated by the competing reaction of dimethylsulfoxide with the hexachloromolybdate(III) ion giving an oxomolybdate species, possibly $MoOCl_5^=$, and dimethyl sulfide, which was easily detected by its characteristic odor. As a result of this reaction DMSO is not suitable for the preparation of completely chelated complexes, but reaction of Na_2H_2-edta and K_3MoCl_6 in DMSO has produced an interesting violet photoactive complex and a considerable amount of alkali halide precipitate. The violet complex is very soluble in DMSO, remaining in solution until all of the solvent is evaporated, at which time it is converted to a yellow precipitate. When $K_3[MoCl_6]$ was allowed to react with the DMSO prior to the addition of the chelating agent only the yellow complex was observed. Purification and characterization of these complexes are still in progress. A red-violet, polymeric complex was obtained when K_3MoCl_6 and 2,2'-dipyridyl were dissolved in DMSO. Carbon:nitrogen mole ratios of less than 4:1 have been obtained rather than the 5:1 ratio expected. The insolubility, non-volatility, and non-stoichiometric composition of the complex has hindered its characterization.

Other molybdenum complexes which have been prepared for use in future synthetic work include molybdenum(IV) chloride, using the method of Austin and Tyree,[13] $K_4[Mo(CN)_4(OH)_4]$ and $K_3[Mo(CN)_4(OH)_3-(H_2O)]$ using the method of Bucknall and Wardlaw.[14] The hydrolysis constant between $K_4[Mo(CN)_4(OH)_4]$ and $K_3[Mo(CN)_4(OH)_3(H_2O)]$ in water has been determined as well as their absorption spectra. An analysis of the spectra is in progress.

From the preceding it is evident that considerable information on molybdenum complexes has been obtained, but that much of the research has been exploratory and that many of the conclusions still lie in the future.

PART II. UNSATURATED β-KETOAMINE COMPLEXES

INTRODUCTION

Although β-diketone complexes have undergone considerable study during the past sixty years, little research on the corresponding unsaturated β-ketoamine complexes had been reported at the time this study was initiated; in fact, only copper complexes had been isolated[15] The interesting isomerism which is possible for these complexes led to a study of the β-ketoamine complexes.

RESULTS

Syntheses of trans-bis-(4-amino-3-pentene-2-ono)-nickel(II) in both aqueous and non-aqueous solution have been developed as well as the ultraviolet, visible, and infrared spectra of this new, red, volatile, diamagnetic, planar complex.[16] The trans-configuration was apparent from the ligand field absorption bands of the spin-paired complex. No evidence for the cis complex has been obtained. (See addendum for details.) Other investigators have recently reported nickel[17] and chromium[18] N-arl derivatives in non-aqueous media, but the failure to obtain complexes in aqueous solution[18] is undoubtedly due to the ease of hydrolysis of the ligands at elevated temperatures.

The low temperature sublimation of the nickel β-ketoamine complex, the successful gas chromatographic separations of β-diketone complexes by Sievers, Moshier, Ponder, and Morris,[19] and the ease of preparation of the nickel(II) chelate has led to a study of β-ketoamine complexes of other metals. The molybdenyl(VI) complex has been discussed in part I of this report. The hydrolysis of β-ketoamines in aqueous solution at elevated temperatures has necessitated the use of either concentrated ammonia or non-aqueous media for reactions much above room temperature, although this has been no problem with labile ions.

The hydrolysis is catalyzed by iron(III) since aqueous solutions of 4-amino-3-pentene-2-one and iron(III) react to give the iron(III) acetylacetonate almost immediately. However, the β-ketoamine complex can be prepared in absolute alcohol. Manganese(II) also appears to catalyze the decomposition of the β-ketoamine, the isolated complex from water being primarily the β-diketone one.

Attempts to simplify the procedure of Collman and coworkers[18] for the chromium complex have been unsuccessful. Concentrated ammonium hydroxide solutions of $[Cr(NH_3)_5Cl]Cl_2$ (prepared by allowing $CrCl_3$ to dissolve in liquid ammonia and subsequent separation from the hexammine in aqueous hydrochloric acid)[20] yielded only chromites insoluble in organic solvents. Suspension of the complex ion in an absolute alcohol solution of the β-ketoamine heated under reflux conditions in an ammonia atmosphere for 36 hours yielded only the starting materials.

Attempts to prepare bis-(4-amino-3-pentene-2-ono)-nickel(II) by bubbling ammonia through a hot benzene solution of nickel acetylacetonate dihydrate were unsuccessful, but some interesting color changes have been observed for analogous reactions of the trifluoroacetylacetonates of copper and cobalt(II). The blue-violet copper solution turned green almost immediately and with excess ammonia a deep blue precipitation occurred. Later experimentation has suggested the first step may involve a diammine of the copper β-diketone complex followed by the preparation of a tetraamminecopper-(II) salt of acetylacetone. The alternative possibility of the β-ketoamine being prepared by copper(II) catalysis cannot be ruled out until pure products have been obtained and analyzed.

4

The ligands 1,1,1-trifluoro-4-amino-3-pentene-2-one and 1-phenylimino-1,3-diphenyl-2-propene-3-one have been prepared for future experimentation by standard condensation methods.

Vapor phase chromatography of the ketoamines has not been attempted. In view of the low sublimation temperature of the nickel complex (85°)[16] success seems quite likely as soon as general methods for preparing the complexes are available.

PART III. TUNGSTEN CHELATES

INTRODUCTION

Very little is known about tungsten chelates other than some tungsten(VI) oxo derivatives which are analogous to the corresponding molybdenum complexes.[22] Several appear more difficult to prepare, apparently because of a greater inertness in the tungsten-oxygen bond of the tungstates. The structures of these are questionable and several appear to exist in more than one stoichiometric ratio. Addition compounds of tungsten(VI) chloride and $WOCl_4$ with some potential chelating amines have been observed.[23] In the study of the reactions of numerous diamines with tungsten(VI) chloride,[23a] the addition of three molecules of the various diamines to each molecule of tungsten(VI) chloride was noted. Although the paper explained this as chelation, most of the diamines were aromatic <u>meta</u> or <u>para</u> diamines which are sterically unable to form chelate rings with a metal ion. Other than this incorrect interpretation of diamine behavior and a tungsten(0) chelate,[24] all other complexes of tungsten contain monodentate groups.

RESULTS

In order to distinguish between the addition compounds of Prasad and Krishnaiah[23a] which are capable of chelate formation and those which are not, the <u>ortho-</u> and <u>para</u>-phenylenediamine complexes of WCl_6 were prepared and their infrared spectra measured in an attempt to elucidate the nature of the coordination in these complexes. Pure WCl_6 was prepared by fractional sublimation of the crude commercial chloride in a dry, oxygen-free atmosphere. Preparative gas chromatography also appears to be a suitable means of separating WCl_6 from the contaminating oxychlorides. The diamines were purified by sublimation just prior to use. Solutions of WCl_6 in dry carbon tetrachloride were allowed to react with dry carbon tetrachloride solutions of the diamines.

The complex $WCl_6 \cdot 3$ <u>o</u>—$C_6H_4(NH_2)_2$ precipitated as a reddish-brown solid and the corresponding <u>para</u> derivative as a green solid. Both are insoluble in most dry organic solvents and decompose in water. The complexes are more stable to air than WCl_6 but decomposition is evident in moist air.

Complexation occurs with both isomers as is indicated by the

5

disappearance and/or shifts in the amine IR peaks as well as the appearance of new peaks associated with coordinated amine groups.

Gas chromatography is unsuitable for purification and characterization as the complexes decompose before attaining an appreciable vapor pressure; i.e., the first vapor detected is that of the parent amine. Undoubtedly some of the chloride on the WCl_6 is ionized during complex formation. The lack of solubility in organic solvents is in agreement with this; however, polymerization would also account for the observed behavior and seems quite likely in the case of the para-phenylenediamine complex.

The only conclusions which could be drawn from the study of the phenylenediamine complexes is the fact that complexation does indeed occur with both amine groups of both isomers and that polymerism must occur in the complex of the para isomer.

For future experimentation on tungsten chelates, $K_3[W_2Cl_9]$, $K_4[W(CN)_8] \cdot 2H_2O$, $K_3[W(CN)_4(OH)_3(H_2O)] \cdot xH_2O$, and $K_4[W(CN)_4(OH)_4] \cdot xH_2O$ have been prepared. The first two were prepared using the new direction of Heintz[25] and the latter two by photohydrolysis of the octacyano complex. This method was chosen over the recent published procedure.[26] An aqueous solution of $[W(CN)_8]^{4-}$ in a Pyrex test tube was subjected to a high intensity mercury lamp until the addition of alcohol to a drop of the solution yielded a blue precipitate of $K_3[W(CN)_4(OH)_3H_2O)] \cdot xH_2O$. Addition of solid alkali to the blue aqueous solution yielded a yellow (or red depending on the concentration) solution and eventually a red precipitate of $K_4[W(CN)_4(OH)_4] \cdot xH_2O$.

It is evident that considerable experimentation on tungsten complexes remains. Some qualitative evidence for tungsten chelates with the above reagents has been obtained, but no definite statements can be made at this time with regard to composition.

REFERENCES

(1) (a) Anon., "Organic Complexes of Molybdenum," Chemical Data Bulletin 9, Climax Molybdenum, New York (1956); (b) G. Spengler and J. Gansheimer, Angew. Chem., $\underline{69}$, 523 (1957); (c) J. G. Dean, H. Kay, and M. L. Larson, "Molybdenum Chelates, Esters, and Organometallics," Advances in Chemistry Series, No 23, Am. Chem. Soc., Washington, D.C., (1959) pp. 357-367.

(2) (a) R. L. Pecsok and D. T. Sawyer, J. Am. Chem. Soc., $\underline{78}$, 5496 (1956); (b) R. E Sievers and J. C. Bailar, Jr., Inorg. Chem , $\underline{1}$, 174 (1962).

(3) D. T Sawyer, private communication.

(4) A. Rosenheim and A. Bertheim, Z. anorg. Chem., $\underline{34}$, 427 (1903).

(5) G. T. Morgan and R. A. S. Castell, J. Chem Soc., $\underline{1928}$, 3252.

(6) (a) Rosenheim and Nernst, Z. anorg. allgem. Chem., $\underline{214}$, 216 (1933); (b) R. J. P. Williams, in S. Kirschner, Ed., "Advances in the Chemistry of the Coordination Compounds," Macmillan, N. Y., 1961, pp. 65-87

(7) F. Gach, Monatsh., $\underline{21}$, 98 (1900).

(8) W C Fernelius and B. E. Bryant, Inorg. Syntheses, $\underline{5}$, 105 (1957), review article.

(9) (a) K. H. Lohmann and R. C Young, Inorg. Syntheses, $\underline{4}$, 97 (1953); (b) W. G. Palmer, "Experimental Inorganic Chemistry," Cambridge University Press, Cambridge, 1959, pp. 413-415.

(10) (a) M. L Larson and F. W. Moore, Inorg Chem., $\underline{1}$, 856 (1962); (b) J. H Balthis, J. Inorg. Nuclear Chem., $\underline{24}$, 1017 (1962).

(11) T. G. Dunne and F. A. Cotton, Inorg. Chem , $\underline{2}$, 263 (1963).

(12) W. C. Fernelius, K. Terada, and B. E. Bryant, Inorganic Syntheses, $\underline{6}$, 147 (1960).

(13) T. E. Austin and S. Y. Tyree, J. Inorg. Nuclear Chem., $\underline{14}$, 141 (1960).

(14) W. R. Bucknall and W. Wardlaw, J. Chem. Soc., $\underline{1927}$, 2981.

(15) (a) A. Combes and C. Combes, Bull. soc. chim. France [3] $\underline{7}$, 781 (1892); (b) H. F. Holtzclaw, Jr., J. P. Collman, and R. M. Alire, J. Am. Chem. Soc., $\underline{80}$, 1100 (1958).

(16) R. D. Archer, Inorg. Chem., $\underline{2}$, 292 (1963), an addendum to this report.

(17) W. Ludwig, Helv. Chim. Acta, $\underline{45}$, 665 (1962).

(18) J. P. Collman and E. T. Kittleman, Inorg. Chem., $\underline{1}$, 499 (1962).

(19) (a) R. E. Sievers, R. W. Moshier and B. W. Ponder, Abstracts 141st National Meeting, American Chemical Society, Washington, 1962, p. 35M; (b) R. E. Sievers, R. W. Moshier and M. L. Morris, Inorg. Chem., $\underline{1}$, 966 (1962); (c) R. E. Sievers, B. W. Ponder, M. L. Morris and R. W. Moshier, preprint of paper entitled "Gas Phase Chromatography of Metal Chelates of Acetylacetone, Trifluoroacetylacetone, and Hexafluoroacetylacetone."

(20) W. E. Henderson and W. C. Fernelius, "A Course in Inorganic Preparations," McGraw-Hill, New York, 1935, p. 130.

(21) D. F. Martin, G. A. Janusonis, and B. B. Martin, J. Am. Chem. Soc., $\underline{83}$, 73 (1961).

(22) P. Pascal, Ed., "Nouveau Traité de Chimie Minérale," Masson et Cie, Paris, Vol. 14, 1959, pp. 993-998.

(23) (a) Prasad and Krishnaiah, J. Indian Chem. Soc., $\underline{37}$, 588 (1960); (b) Ibid., $\underline{38}$, 183 (1961).

(24) J. Chatt and H. R. Watson, Nature, $\underline{189}$, 1003 (1961).

(25) E. A. Heintz, Inorg. Syntheses, $\underline{7}$, 142 (1963).

(26) K. N. Mikhalevich and V. M. Litvinchuk, Zhur. Neorg. Khim., $\underline{4}$, 1775 (1959).